

Electrochemical and hydrodynamic Interferences on the Performances of an Oxygen Microsensor with Built-in Electrochemical Microactuator*

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Summary

A concept of novel electrochemical *in situ* self-calibration technique for an oxygen microsensor has been proposed to devise a convenient calibration method without an externally coupled apparatus¹. Systematic investigations on the influences of various electrochemical (pH) and hydrodynamic (solution stirring) conditions on the proposed microsensor performances are presented. The results suggest that (1) the calibrating microenvironments can be manipulated with carefully engineered sensor designs and optimized generating signals, and (2) the external oxygen permeable membrane is needed to minimize the electrochemical and hydrodynamic interferences.

Motivation

The importance of continuous chemical monitoring cannot be overemphasized to realize autonomous and unattended instrumentation. A dependable self-calibration method is required to achieve reliable biochemical sensor system². The proposed method addresses a novel *in situ* self-calibrating oxygen microsensor based on water electrolysis by using an integrated electrochemical actuator (generating electrode, GE)¹ (Fig. 1). This technique is expected to enable periodic *in situ* self-calibration and self-diagnosis of microsensor during real-time oxygen monitoring and will lead to intelligent devices with on-board, self-calibration features.

Results

We designed and fabricated polarographic oxygen microsensors on a flexible Kapton[®] (polyimide) substrate. A potentiostat and a constant current source were used to bias the microsensor (three-electrode cell) and to provide generating signal to GE, respectively (Fig. 2). The actuation procedure involved an oxygen-generating phase during sensor operation. The chronoamperometric responses increased during the oxygen-rich phase, and then gradually returning to the original level of air-saturated solution (Fig. 3a). In a strong pH buffer solution the sensor showed much diminished oxygen responses during this phase (Fig. 3b). In both cases the responses exceeded those in the oxygen-saturated solution. These imply the effect of bulk pH on the catalytic activity of cathodic oxygen reduction due to the local pH change accompanied by water electrolysis. Stirring of the solution reduced the oxygen responses by disturbing the local microenvironment as expected (Fig. 3c). The responses during the oxygen-depletion phase approached to that in the nitrogen-saturated (oxygen-depleted) solution (Fig. 3d).

1. C. S. Kim, J. O. Fiering, C. W. Scarsboro, H. T. Nicks, "A novel *in situ* self-calibration method for an oxygen microsensor," World Congress on Medical Physics and Biomedical Engineering, Chicago, 2000.

2. P. Yager, "Biomedical sensors and biosensors," in B. E. Ratner, et al. (eds), Biomaterials Sciences, Academic Press, 1996.

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Figure 1. Concept of an electrochemical *in situ* self-calibration of oxygen microsensor. Microsensor can be confined in a controlled microenvironment during the oxygen-saturation and oxygen-depletion phases depending on the polarity of generating electrode (GE).

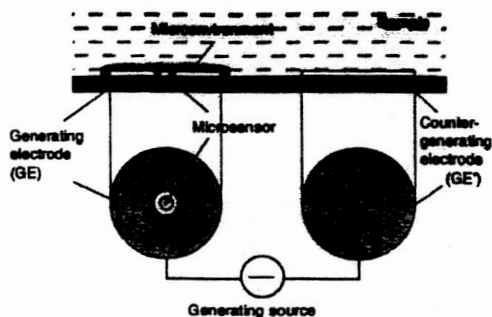


Figure 2. Measurement scheme for chronoamperometric responses. A potentiostat is employed for the 3-electrode oxygen microsensor, a constant current source for generating microenvironments, respectively.

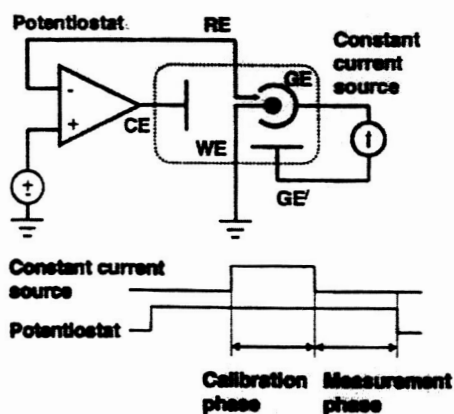
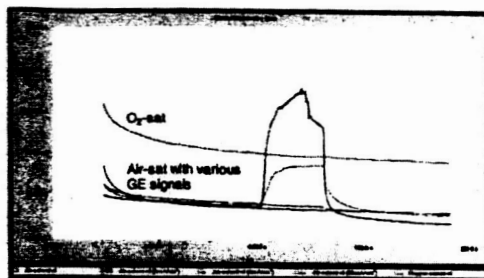
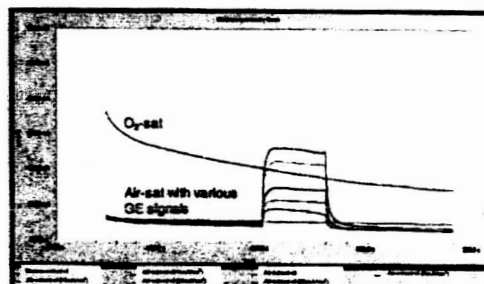


Figure 3. Changes in oxygen microenvironment around the microsensor manipulated by the surrounding generating electrode; chronoamperometric responses during the oxygen-generating phase with various generating current signals compared with that in oxygen-saturated solution (top curve) (a) in an air-saturated plant nutrient solution (quarter strength Hoagland solution), (b) in an air-saturated phosphate buffer solution, (c) in an air-saturated vigorously-stirred phosphate buffer solution; chronoamperometric

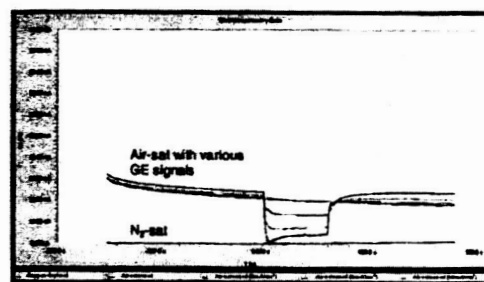
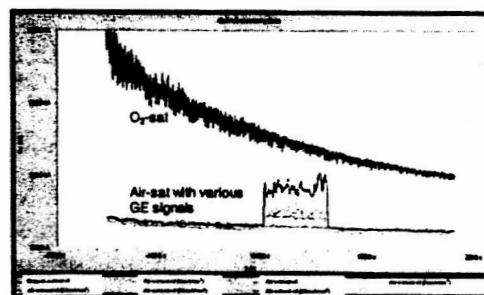
responses during the oxygen-depleting phase with various generating current signals compared with that in nitrogen-saturated solution (bottom curve) (d) in an air-saturated phosphate buffer solution.



(a)



(b)



(d)

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Electrochemical and Hydrodynamic Interferences on the performance of an Dissolved Oxygen Microsensor with Built-in Electrochemical Actuator

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Built-in, on-chip intelligence of biochemical microsensor

- Intelligent microsensor system; unattended, autonomous, self-adaptive, self-regulatory.
- Functional integration as well as structural integration.
- On-chip integration of "biochemical actuation" system to establish dynamic microenvironments.

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Necessity of "In situ self-diagnosis and/or self-calibration"

- Periodic correction of slope/ baseline drift, diagnosis of functionality.
- Little *in situ* self-diagnosis and/or self-calibration feature in commercially available sensors.
- One of key obstacles for realization of reliable biochemical sensor for continuous use.

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Dissolved oxygen microsensor with in situ self-diagnosis capability

- Microenvironments established by water electrolysis.
- O_2 -rich or O_2 -depleted phases according to anodic or cathodic behavior of actuating electrode (AE).

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Microfabrication of 3-electrode amperometric microsensor

- Substrate: Kapton (polyimide)
- Metal deposition (Pt)
- Photoresist lithography
- Metal etching
- Polyimide lithography (thin)
- Polyimide lithography (thick)

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Instrumentation and operation modes

- Electrically-floated operation of a potentiostat and a galvanostat.

Mode 1

Actuating phase Diagnosis phase

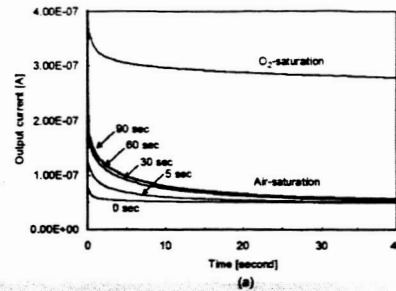
Mode 2

Actuating phase Diagnosis phase

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Transient sensor responses after O_2 -generating actuation phases of various duration (mode 1)



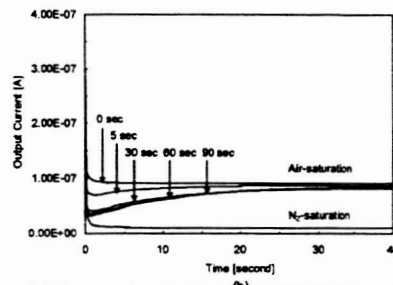
- Initial values approaching that of O_2 -saturation; O_2 -rich microenvironments (actuating current density: 5 mA/cm^2).
- Convergence to background response; being equilibrated with surrounding medium shortly.

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Transient sensor responses after O_2 -depleting actuation phases of various duration (mode 1)



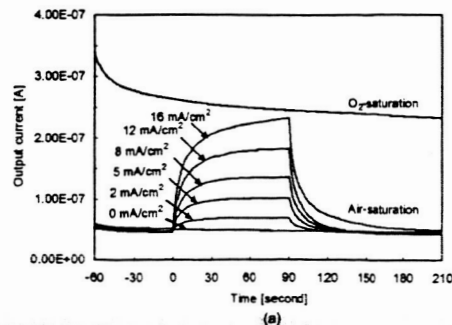
- Initial values approaching that of N_2 -saturation; O_2 -depleted microenvironments (actuating current density: 5 mA/cm^2).
- Convergence to background response; being equilibrated with surrounding medium shortly.

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Steady-state responses during O_2 -generating actuation phases of various current density (mode 2)

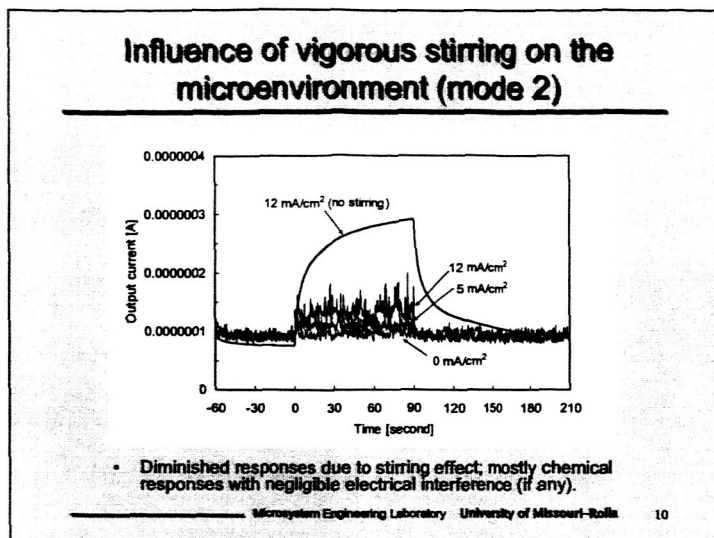


- Approaching to O_2 -saturation value with increasing actuation current density.

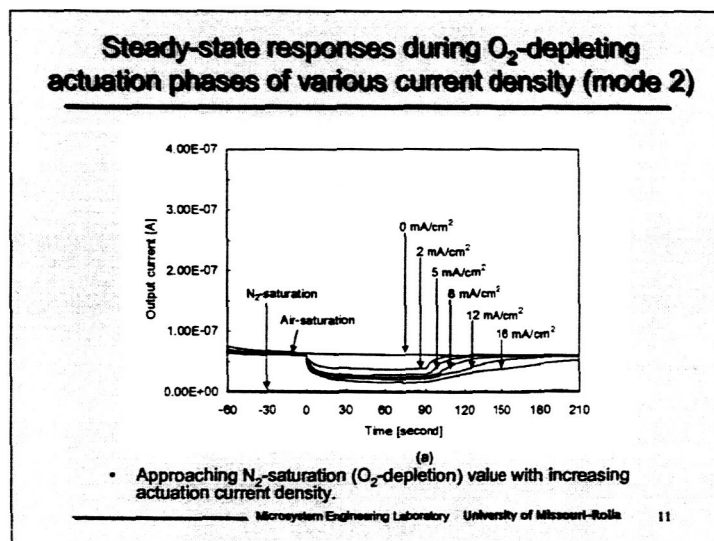
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What is going on in the microenvironment?

- Super-saturation; excessive solubility of electrochemically generated dissolved gas.
- Dependence of sensitivity on pH; coefficient = 2 (high pH) ~ 4 (low pH).
- Concentration-driven convection of oxygen; from AE to WE.
- "Feedback" of H₂O₂; from WE to AE.
- Local temperature elevation; actuation current density.

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Conclusion and future works

- Controlled oxygen microenvironments with an integrated actuator to provide an on-chip intelligence.
- Need of an external membrane to minimize the electrochemical/hydrodynamic interferences.
- Microfluidic structures for further manipulations to achieve *in situ* self-calibration.
- Applicable to integrated optical sensing platform.

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